Surface-enhanced Raman scattering from magneto-metal nanoparticle assemblies

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1. Introduction

Noble metal nanoparticles are ideal substrates for surface-enhanced Raman scattering (SERS) due to their intrinsic properties of collective oscillation of free electrons on the metal surface excited by an incident light, known as localized surface plasmon resonance (LSPR) [1–3]. Au nanoparticles have attracted more attention because of their chemical inertness, and have been widely used as SERS substrates in the field of biochemistry, biosensing and environmental monitoring. The size and shape of Au nanoparticles [4,5] and the amounts of “hot spots” [6,7] can highly influence the SERS effect. In addition, when two metallic nanoparticles are in close proximity, their dipole coupling may lead to enhancement factors as high as $10^{15}$. Magnetic nanoparticles have been extensively investigated for their potential applications in tissue imaging [8], drug delivery [9] and information storage [10]. Fe$_3$O$_4$ nanoparticles are one type of commonly studied nanomagnetic iron oxides due to their good biocompatibility, strong superparamagnetic property, low toxicity, easy preparation and high adsorption ability [11,12]. Considered advantages from the components and structure, the Fe$_3$O$_4$ core@Au shell (Fe$_3$O$_4$@Au) nanoparticles can be stable in corrosive conditions and can be easily modified with thiol group [13] and amino group [14] by the coating of Au shells, and can be controlled moving in fluid and collected in magnetic field through the impact of Fe$_3$O$_4$ cores. These nanoparticles can be used as probes for ultrasensitive detection and have
the potential to promote the detection sensitivity and reproducibility. At the same time, the Fe3O4@Au nanoparticles can be used as optical contrast agents under magneto motive imaging conditions [15] and substrates for surface plasmon resonance (SPR) imaging [16,17] and two photon fluorescence imaging [18] by the optical activities of Au shells.

In this paper, we report the facile synthesis of magneto-metal nanoprobes composed of a Fe3O4 core and an Au nanoshell. In contrast to the previous reports that prepared Au-coated magnetic nanoparticles either from γ-Fe2O3 or oxidized Fe3O4 cores [19], or in organic solvents [20], our strategy successfully coated freshly prepared Fe3O4 cores with Au shells and the whole process was carried out in aqueous condition. Subsequently, the Fe3O4@Au nanoparticles were assembled into SERS substrate by magnetic-directed assembly using p-thiocresol as reporter molecule, from which a significantly enhanced SERS signal is attained.

2. Experiment

2.1. Materials

The iron(II) sulfate heptahydrate (FeSO4·7H2O), iron(III) chloride hexahydrate (FeCl3·6H2O) and trisodium citrate dihydrate (C6H5Na3O7·2H2O) were purchased from Sinopharm Chemical Reagent Co. Ltd. The ethanol and ammonia solution (25.0–28.0%) were purchased from Beijing Chemical Works. The above reagents were all of analytical grade. The chloroauric acid (AuCl4·HCl·4H2O) was purchased from Shenyang Jinke Chemical Reagent Factory. The SERS analyte molecule p-thiocresol (C6H5S, purity 98%) was purchased from Alfa Aesar. All of the chemicals were used as received.

2.2. Preparation of Fe2O4, Fe3O4@Au and Au nanoparticles

The Fe3O4 nanoparticles were prepared via co-precipitation reaction [21,22]. Typically, 3.3361 g of FeSO4·7H2O (0.012 mol) and 3.2436 g of FeCl3·6H2O (0.012 mol) were dissolved in 250 mL of deionized water. The water was previously bubbled with N2 and the whole process was carried out under N2. An amber and transparent solution was obtained after stirring and the molar ratio of Fe2+ to Fe3+ was 1. Then 9 mL of NH3·H2O was added rapidly at room temperature, and the solution turned black-green and turbid immediately. The mixture was stirred for 30 min at room temperature, heated to 80 °C and kept for 30 min, and then cooled to room temperature naturally. A black suspension was obtained and the deposit was separated by magnetic decantation. The precipitated particles were rinsed with deionized water until the separated liquid became neutral. Finally, the Fe3O4 nanoparticles were ultrasonically dispersed in 200 mL of 0.1 M sodium citrate solution to form a suspension.

The Fe3O4@Au nanoparticles were prepared through the reduction of HAuCl4 in the presence of Fe3O4 nanoparticles. In a typical synthesis, 0.1 mL of Fe3O4 nanoparticles suspension was added to 100 mL of 1 M sodium citrate solution. The mixture was sonicated for 30 min and stirred at 80 °C for 6 h. Then 100 μL of 0.01 M HAuCl4 solution was injected every 2 min. The thicknesses of Au shells can be controlled by changing the amount of HAuCl4. The suspension was vigorously stirred for another 30 min at 80 °C after the accomplishment of reagents injection, then continually stirred for 2 h and cooled to room temperature naturally. After placing at room temperature for one night, the mixture was sonicated for 5 min and a claret suspension was produced. The solid was rinsed with deionized water and separated by magnetic decantation for 3 times to remove the nonmagnetic Au nanoparticles. Finally, the Fe3O4@Au nanoparticles were ultrasonically dispersed in 20 mL of deionized water to form a suspension.

2.3. Raman experiments

The schematic illustration of the surface modification and magnetic separation of labeled Fe3O4@Au nanoparticles is shown in Scheme 1. The p-thiocresol (p-TC, also known as 4-methylbenzenethiol) was used as Raman reporter molecule. For the preparation of SERS samples, 1 mL of Fe3O4@Au or Au nanoparticles suspension was added to 10 mL of deionized water. Then 10 μL of p-TC ethanol solution (at the concentration of 1 μM or less) was injected to the diluted suspension and the dispersion was stirred at room temperature for 24 h. The thiol group in the molecule can be strongly adsorbed on the gold surface through the chemical bound between the sulfur atom and the gold atom. The resulting nanoparticles were centrifuged and washed with water and ethanol several times to remove the excess reagents, and then re-suspended in 500 μL of deionized water and transferred onto a piece of watch-glass. Finally the Raman-labeled Fe3O4@Au nanoparticles were enriched by a magnet and the water was carefully withdrawn, while the Raman-labeled Au nanoparticles were left to dry completely.

All Raman experiments were performed with a Renishaw Micro-Raman Spectroscopy System. SERS spectra were measured using a 50× microscope objective. An excitation wavelength of 633 nm was applied in all measurements. The watch-glass with labeled Fe3O4@Au or Au nanoparticles was directly used for SERS substrates and the laser can be easily focused on the aggregation of nanoparticles.

2.4. Characterization

The samples were characterized by X-ray powder diffraction (XRD) studies, using a Japan Rigaku D/max-TTRIII with Cu Kα radiation. XRD patterns were obtained for 20–90° by step-scanning with a step size of 0.2° and a scanning rate of 5° min⁻¹. Photomicrographs were obtained from a USA FEI Tecnai G² 20 S-TWIN transmission electron microscope (TEM), using an accelerating voltage of 200 kV. Magnetic measurements were carried out using a USA Quantum Design PPMS-9 physical property measurement system (PPMS) with fields up to 9 T at 300 K.

3. Results and discussion

Fig. 1 gives the XRD patterns of Fe3O4 and Fe3O4@ Au nanoparticles. The diffraction peaks at 2θ = 30.0°, 35.3°, 43.0°, 53.4°, 56.9°, and 62.5° in curve a could be attributed to the (220), (311), (400), (422), (511), and (440) planes of Fe3O4 in a cubic phase [23], while the diffraction peaks at 2θ = 38.1°, 44.2°, 64.5°, 77.5°, and 81.6° in curve b could be indexed as the (1 1 1), (2 0 0), (2 2 0), (3 1 1), and
Fe3O4@Au magnetic nanoparticles

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Fe3O4 are very weak in curve b, which is dissimilar to the other report [25]. Because the Fe3O4@Au product was obtained using magnetic decantation, the Fe3O4 particles must exist in sample, so the peaks of Fe3O4 are considered being concealed by the intense diffraction peaks of Au.

Fig. 2(a) shows the TEM images of Fe3O4@Au nanoparticles. There is a strong contrast difference in all of the nanoparticles. The light ones are bare Fe3O4 nanoparticles, with a diameter about 10 nm. Because there are hardly simple Au nanoparticles in existence, the dark ones must be Fe3O4@Au nanoparticles, the size of which ranges from 17 nm to 30 nm. The changes of TEM contrast and particle size indicate the core-shell structure. The Au nanoparticles synthesized using a similar procedure is distributed at 15 ± 3 nm.

The hysteresis loops of the bare and coated Fe3O4 nanoparticles are illustrated in Fig. 3. The saturation magnetization values are found to be about 80.0 emu g⁻¹ and 7.4 emu g⁻¹ for Fe3O4 and Fe3O4@Au nanoparticles, respectively. The saturation magnetization of Fe3O4@Au is much smaller than that of Fe3O4, which is due to the diamagnetic contribution of the thick Au shells surrounding the magnetic cores. There is no reduced remanence and coercivity being zero existed, indicating that the two samples are superparamagnetic. That means, when the external magnetic field is removed, the nanoparticles can be relatively well dispersed.

Fe3O4@Au nanoparticles have been recently used in SERS investigation [26–28]. Here the p-thiocresol is chosen as Raman reporter molecule. The p-TC is an aromatic thiol that forms self-assembled monolayers (SAMs) on gold, silver, and copper [29,30], but hardly interacts with Fe3O4. In addition, it is well known that Fe3O4 nanoparticles do not show SERS property, we can therefore conclude that the SERS results from Fe3O4@Au nanoparticles would not be significantly influenced by the uncoated Fe3O4 cores coexisted.

Fig. 4 displays a series of SERS spectra of p-TC molecules on the Fe3O4@Au nanoparticles. The tortuous curve (a) from Fe3O4@Au nanoparticles only shows some very weak vibrational peaks corresponding to magnetite [31]. When the Fe3O4@Au nanoparticles are labeled with p-TC, significant SERS spectra of p-TC molecules with a strong characteristic vibrational peak at 1070 cm⁻¹ can be acquired. The labeled nanoparticles have been thoroughly rinsed with ethanol and water to remove multilayers and free molecules, so the p-TC concentrations on nanoparticles should be equal to or less than a monolayer. It is evident that the Raman intensity decreases with decreasing the amount of p-TC. In early reports, the Raman substrates were usually soaked in a p-TC solution to form
The nanoparticles are concentrated and fixed on the watch-glass after drying, so the intensity and repeatability of Raman signal is improved. Particularly the labeled Fe$_3$O$_4$@Au nanoparticles can be gathered by the effect of magnetic field, more probes with reporter molecules can be incorporated under laser spot, so the sensitivity and reproducibility is better than the case of Au nanoparticles.

At the same time, resulting from the aggregation of Fe$_3$O$_4$@Au nanoparticles, the smaller interparticle gaps can support extremely intense local electromagnetic fields known as “hot spots” [6,34], which give rise to the enormous SERS enhancement. Additionally, it has been reported that the formation of “hot spots” may cause the trapped analytes to change molecular orientation [7]. Although our research is unconcerned with detailed spectral analysis, based on the more abundant “hot spot” generated than the other cases, the Fe$_3$O$_4$@Au nanoparticles may be potential probes for SERS fingerprint analysis.

4. Conclusions

In summary, we have prepared Fe$_3$O$_4$@Au composite nanoparticles by a facile process and use the particles as ultrasensitive probes for SERS. Based on the surface-active Au shells and superparamagnetic Fe$_3$O$_4$ cores, the particles can be easily modified and then separated in a magnetic field, which makes them useful for a variety of applications where separation of the particles adsorbing analytes is required. SERS studies with excitation at 633 nm showed significant enhancement with excellent reproducibility to detect less than monolayer concentrations of p-TC, and the non-optimized detection limit was estimated to be as low as 4.55 pM p-TC ethanol–water solution. Because more labeled probes and “hot spots” can be incorporated under laser spot by this method, the detection sensitivity and reproducibility of SERS with Fe$_3$O$_4$@Au nanoprobes is superior to the cases with Au nanoparticles.

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References

[23] JCPDS Card, File No. 75-1610.